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A NEW VOLUMETRIC METHOD FOR THE DETERMINATION OF MERCURY.

A VOLUMETRIC METHOD FOR THE DETERMINATION OF HYDRAZINE.

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Art. XXXI.—*A New Volumetric Method for the Determination of Mercury*; by George S. Jamieson.

Among the methods that have been proposed for the volumetric determination of mercury, the titration in nitric acid solution by means of ammonium thiocyanate,[*] according to Volhard's method for silver, while it appears to be very accurate, is not generally applicable because it cannot be used in the presence of chlorides. The method of Rupp[†] consists in adding potassium iodide and an excess of sodium hydroxide to any mercuric solution, then precipitating the finely divided metal by means of formaldehyde, and, after acidifying with acetic acid, dissolving the metal with standard iodine solution and titrating back with sodium thiosulphate. This method is simple and rapid, and while it seems to be a good one for small quantities of mercury, my experience with it is that it gives seriously low results with amounts of mercuric chloride as large as 0·1 to 0·2 grams. Hempel's method,[‡] which consists in titrating mercurous chloride (or iodide) with iodine and thiosulphate, is undoubtedly very accurate, if it is used with proper precautions to completely dissolve the mercurous chloride in the iodine solution.[§]

The method to be described is based upon the titration of mercurous chloride with potassium iodate in the presence of 15 to 20 per cent of actual hydrochloric acid and a small volume of an immiscible solvent, such as chloroform. This general method of titration is the well known one of L. W. Andrews,[‖] but as far as is known it has not been applied previously to the titration of mercurous chloride. It has the advantage over Hempel's method in requiring only a single, very stable volumetric solution, instead of two solutions which cannot be preserved for a long time unchanged, while the method of titration appears to be no less exact. It is to be observed that the iodate titration cannot be applied to mercurous iodide without the employment of an entirely different factor, since the iodine would affect the results.

It has been found that mercurous chloride reacts with potassium iodate according to the theoretical requirements of the equation

$$4HgCl+KIO_3+6HCl=4HgCl_2+KCl+ICl+3H_2O$$

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[*] Cohn, Berichte, xxxiv, 3502: Rupp, ibid., xxxv, 2015.

[†] Ibid., xxxix, 3702.

[‡] Sutton, 10th edition, p. 263.

[§] Smith, Chem. News, cv, 14.

[‖] Jour. Amer. Chem. Soc., xxv, 756, 1903.

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In order to test the method, a solution of potassium iodate was standardized with pure sublimed iodine, using Andrews' titration under the same conditions as are described beyond for the mercurous chloride titration.

	Iodine taken	KIO_3 used	Wt. of I for 1^{cc}
A	·1003^g	11·8^{cc}	·00848^g
B	·1998	23·6	·00846
Average .	....	....	·00847

Since the reaction in the case of iodine is represented by the equation

$$4I + KIO_3 + 6HCl = KCl + 5ICl + 3H_2O$$

the strength of the potassium iodate solution was $1^{cc} = ·01572^g$ of HgCl.

For the following titrations a sample of pure mercurous chloride which had been dried at 130°–135° C. for several hours and well pulverized was used. The titrations were carried out in a glass stoppered bottle of 250^{cc} capacity in the presence of 20^{cc} of water, 30^{cc} of concentrated hydrochloric acid, and 6^{cc} of chloroform, with thorough shaking of the closed bottle between the additions of the potassium iodate solution. As is usual in such titrations, the chloroform globule at first increases in iodine color and then this color is gradually removed. The end-point is the disappearance of this violet color. It was observed that dried mercurous chloride reacts more slowly in this operation than the precipitated substance which was titrated without drying in some of the experiments to be described beyond, so that in this case very thorough shaking and occasional crushing of the lumps with a glass rod were required. The following table gives the results of the titrations:

	HgCl taken	KIO_3 cc.	HgCl found	Error
I	·4999^g	31·80	·4999^g	·0000^g
II	·5000	31·80	·4999	·0001
III	·5005	31·80	·4999	—·0006
IV	·6001	38·15	·5997	—·0004
V	·4999	31·80	·4999	·0000

The results show a very satisfactory agreement among themselves and with theory.

Since most kinds of organic matter do not interfere with this method of titration, it is applicable to various mixtures containing calomel. It was tried with calomel tablets containing milk sugar, after pulverizing several tablets to obtain a uniform mixture. Quantitative determinations of the calomel were also made by treating portions of the substance with water slightly acidified with hydrochloric acid and weighing the washed and dried residue. The following results were obtained :

Substance taken	KIO_3 used	HgCl found
·4811^{g}	16·50^{cc}	53·91%
·6783	23·25	53·89
·1976	gravimetric	53·94
·5694	"	54·00

The method was applied also to the determination of mercury in a mercuric compound by converting the latter into mercurous chloride and then titrating. For this purpose weighed portions of mercuric chloride were dissolved in warm water with the addition of a few drops of hydrochloric acid; an excess of phosphorous acid solution was then added, and after thorough stirring the precipitate in each case was allowed to settle for about twelve hours. It was then collected on a filter paper and well washed with cold water. The precipitate with the paper was put into the titration bottle, and any precipitate adhering to the beaker and stirring rod was collected by wiping with a piece of filter paper and also put into the bottle. The titrations were carried out as previously described with the following results: (1^{cc} KIO_3 = ·013354^{g}Hg)

No.	$HgCl_2$ taken	KIO_3 sol. used	Hg found	Hg calc.	Error
I	·3934^{g}	21·7^{cc}	·2898^{g}	·2904^{g}	—·0006^{g}
II	·3107	17·2	·2297	·2294	+·0003
III	·4903	27·1	·3619	·3619	·0000
IV	·3315	18·3	·2444	·2447	—·0003
V	·3407	18·8	·2511	·2515	—·0004

The results show that the method is an accurate one.

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Art. XXXII.—*A Volumetric Method for the Determination of Hydrazine;* by George S. Jamieson.

A method for the determination of hydrazine has been described by Rimini* and recently tested further by Hale and Redfield.† This is based upon the oxidation of the hydrazine compound in aqueous solution by the addition of an excess of standard potassium iodate solution, according to the following equation:

$$5(N_2H_4.H_2SO_4) + 4KIO_3 = 5N_2 + 12H_2O + 2I_2 + 2K_2SO_4 + 3H_2SO_4$$

The liquid is then boiled until the iodine is expelled and the excess of potassium iodate is found after cooling by adding potassium iodide, acidifying with sulphuric acid, and titrating with sodium thiosulphate solution. The chief objection to this method, according to Hale and Redfield, is the length of time required for the analysis.

The method to be described here is based upon the titration of hydrazine by potassium iodate in a strong hydrochloric acid solution, according to the general method of L. W. Andrews.‡ It has the advantages of being rapid, and requiring the use of only a single, very stable volumetric solution. Besides, as will be seen from the results that follow, it is very accurate.

In order to test the method, a solution containing 3·567 g. of KIO_3 in 1000^{cc} was prepared. According to the equation of the expected reaction

$$N_2H_4.H_2SO_4 + KIO_3 + 2HCl = N_2 + ICl + 3H_2O + KCl + H_2SO_4$$

the equivalent of this solution is 1^{cc} = ·002169 g. $N_2H_4.H_2SO_4$ and 1^{cc} = ·000534 g. N_2H_4. Weighed portions of pure hydrazine sulphate were placed in a 250^{cc} glass stoppered bottle together with 20^{cc} of water, 30^{cc} of hydrochloric acid and 6^{cc} of chloroform. Then the potassium iodate solution was run in gradually, with shaking between the additions, until the chloroform, after increasing and then diminishing in color, was just decolorized. The following results were obtained:

	$N_2H_4.H_2SO_4$ taken	KIO_3 used	$N_2H_4.H_2SO_4$ found	Error
I	·0487^{g}	22·5^{cc}	·0488^{g}	+·0001
II	·0434	19·9	·0432	—·0002
III	·0589	27·3	·0592	+·0003
IV	·0472	21·9	·0475	+·0003
V	·0986	45·65	·0990	+·0004
VI	·1060	49·00	·1063	+·0003

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* Gazz. chim. ital., xxix, I, 265, 1899.

† Journ. Amer. Chem. Soc., xxxiii, 1362, 1911.

‡ Journ. Amer. Chem. Soc., xxv, 756, 1903.

Determinations of hydrazine in the sparingly soluble double sulphates of zinc, cobalt, nickel, and cadmium were made in order to test the method further. The double salts were prepared by mixing hot solutions of the component sulphates in the presence of a little sulphuric acid, and after digesting for some time on the steam-bath, the crystalline products were filtered off by suction, washed with cold water and dried at 100° C. The titrations were carried out in the same way as described above in the case of the simple sulphate. It was observed that the nickel salt reacted very slowly, apparently on account of difficult solubility, while the other compounds were titrated about as readily as hydrazine sulphate alone.

The following results were obtained:

	Substance	KIO_3 used	N_2H_4 found	Calculated
$ZnSO_4(N_2H_4)_2.H_2SO_4$	·1163^g	43·2^{cc}	19·83%	19·81%
"	·0880	32·6	19·77	"
$CdSO_4(N_2H_4)_2.H_2SO_4$	·1591	51·25	17·21	17·29
"	·1396	45·10	17·25	"
$NiSO_4(N_2H_4)_2.H_2SO_4$	·0692	26·30	20·29	20·23
"	·0890	33·80	20·28	"
$CoSO_4(N_2H_4)_2.H_2SO_4$	·1308	49·20	20·09	20·20
"	·1059	39·70	20·02	"

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